Phonons in Electronic Transport in Nanoscale Systems

Lecture Notes
Caltech NEMS Summer School, 2007

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July 5, 2007

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1. SINGLE PHONON MODES

1.1 Introduction

Mechanical vibrations are described as a collection of normal modes. When these are quantized, we obtain phonons - very similar to the single harmonic oscillator. Phonons are thus quantum excitations. A single phonon can involve billions of atoms, i.e. all those forming the original normal mode.

In bulk materials, one usually finds a whole spectrum of normal modes, characterized by a *dispersion relation*

$$\omega = \omega(\mathbf{k}), \tag{1.1.1}$$

where $\mathbf{k}$ is a label for the normal mode (usually a d-dimensional wave vector, were d is the dimension of the vibrating system), and ω is the angular frequency of the normal mode (two pi times the frequency). We will deal with bulk phonons in the second part of this Lecture.

Sometimes certain normal modes of a vibrating system are particularly interesting, for example the fundamental (lowest) vibration mode in a small beam or a string, or a vibration mode in a molecule. Often such vibrations are observed by interaction with other quantum objects, for example phonons (light) or electrons.

The interaction between electrons and phonons is, needless to say, of key importance for our understanding of a broad variety of physical phenomena such as superconductivity, thermal conductance, electrical resistance, and decoherence, just to name a few. The chapter ‘electron-phonon interactions’ thus forms part of any good textbook on, e.g., solid state physics (such as ‘Ashcroft/Mermin’ just for the sake of naming one...).

The interactions between electrons and phonons are however also a paradigm for what one would call interactions between massive particles and gauge bosons in particle theory. I am interested in the ‘cleanest’ possible kind of such interaction, and that is why the subject of this first Lecture is the interaction between single electrons and single phonon modes. At first sight, this might perhaps look somewhat artificial but we will soon see that some of the most exciting, recent experiments in nanomechanics, molecular electronics, and mesoscopic physics are just about this idea.

1.2 A Simple Model Hamiltonian

Rather than giving an overview of recent experiments with single phonon modes, I want to move directly to the definition of the simple model mentioned above. It describes electrons tunneling between a left and a right lead (electron reservoir $\mathcal{H}_{\rm res}$) through a single molecular level ε that is coupled to a single phonon mode with creation operator $a^\dagger$. The total Hamiltonian (system plus coupling to leads) is

$$\mathcal{H} \;=\; \mathcal{H}_S + \mathcal{H}_V + \mathcal{H}_{\rm res} \tag{1.2.1}$$

The system Hamiltonian $\mathcal{H}_S$ describes a single molecular level ε (we will sometimes call it 'dot') linearly coupled to a single harmonic oscillator mode,

$$\mathcal{H}_S = \omega_0 a^\dagger a + \lambda\omega_0(a + a^\dagger)n_d + \varepsilon n_d + \frac{U}{2}n_d(n_d - 1). \tag{1.2.2}$$

where n_d is the electronic number operator. The term with U mimicks the Coulomb interaction between two electrons with spin up and sin down on the level. In the following, we assume that only one electron can occupy the molecular level, corresponding to the limit $U \to \infty$. We also assume that the spin of the electron plays no role here - this is a little bit artificial as the electron spin does play a role usually. We could imagine, for example, that the electrons are all spin-polarized in a very strong magnetic field. The point is that we really want to focus on the electron-phonon interaction here and therefore do not wish to include any additional interaction effects in our mdel. In the following we will stick with spin-polarized electrons (e.g., all electrons with spin $\uparrow$) and omit the spin label. As we have only $n_d = 0$ or $n_d = 1$ electrons on the dot, we shall drop the term $\frac{U}{2}n_d(n_d - 1)$ from now on. The electron number operator on the dot is

$$n_d = d^\dagger d = |1\rangle\langle 1|, \quad d \equiv \hat{s} \equiv |0\rangle\langle 1|, \tag{1.2.3}$$

where d is the annihilation operator for the electron on the dot and we used an equivalent representation in Dirac bra-ket notation with $|0\rangle$ denoting the empty and $|1\rangle$ denoting the occupied dot state, writing d as a projector (for which we reserve the symbol $\hat{s}$).

The electron reservoir term is simple,

$$\mathcal{H}_{\rm res} \equiv = \sum_{k,\alpha=L/R} \varepsilon_{k,\alpha} c^\dagger_{k\alpha} c_{k\alpha}, \tag{1.2.4}$$

describing a gas of free spin-polarized electrons in the left and right reservoir. Finally, the tunnel coupling between the reservoir and the dot is

$$\mathcal{H}_V \;=\; \sum_{k\alpha}(V_{k\alpha} c^\dagger_{k\alpha}\hat{s} + H.c.), \quad \hat{s} \equiv |0\rangle\langle 1|. \tag{1.2.5}$$

Here and in the following, we always set $\hbar = 1$.

1.2.1 System Hamiltonian

We first focus on the system Hamiltonian.

Harmonic Oscillator

The vibrational part of the eigenstates for $n_d = 0$ are the usual harmonic oscillator states

$$H_0|n\rangle_0 = n\omega_0|n\rangle_0, \quad H_0 \equiv \omega_0 a^\dagger a, \tag{1.2.6}$$

which are n-phonon states corresponding to a vibrational energy $n\omega_0$ (we shifted the energy scale such that the $\frac{1}{2}\hbar\omega_0$ from the ground state energy no longer appears).

Shifted Harmonic Oscillator

For $n_d = 1$, the vibrational part of $\mathcal{H}_S$ describes a shifted harmonic oscillator,

$$\begin{aligned} H_\lambda &\equiv \omega_0 a^\dagger a + \lambda\omega_0(a + a^\dagger) = \omega_0 b^\dagger b - \omega_0\lambda^2 & (1.2.7)\\ b &\equiv a + \lambda, \quad b^\dagger \equiv a^\dagger + \lambda, & (1.2.8)\end{aligned}$$

where we introduced shifted ladder operators b and $b^\dagger$ (note that $[b, b^\dagger] = 1 = [a, a^\dagger]$). The operators a and b are related by a unitary transformation,

$$b = a + \lambda = X_\lambda a X_\lambda^\dagger, \quad X_\lambda \equiv e^{\lambda(a - a^\dagger)}, \tag{1.2.9}$$

which is shown by a nested commutator expansion (see below). The operator X_λ is called *unitary displacement operator*. We use it to unitarily transform the unshifted Hamiltonian H_0 into the shifted Hamiltonian H_λ,

$$X_\lambda H_0 X_\lambda^\dagger = H_\lambda + \omega_0\lambda^2 = \omega_0 b^\dagger b. \tag{1.2.10}$$

The eigenstates of H_λ are given by shifting those of H_0,

$$H_0|n\rangle_0 = n\omega_0|n\rangle_0 \quad \rightsquigarrow H_\lambda X_\lambda|n\rangle_0 = [n\omega_0 - \omega_0\lambda^2]X_\lambda|n\rangle_0, \tag{1.2.11}$$

which means that the eigenstates of H_λ are shifted oscillator states

$$|n\rangle_\lambda = X_\lambda|n\rangle_0 \tag{1.2.12}$$

with energies $n\omega_0 - \omega_0\lambda^2$. In particular, the groundstate of H_λ is a *coherent state* in the basis of the unshifted oscillator with energy

$$\varepsilon_0 = -\omega_0\lambda^2. \tag{1.2.13}$$

EXERCISE: Why is the ground state energy of the shifted oscillator smaller than the ground state energy of the unshifted oscillator? Hint: draw a picture of the oscillator potential in the position representation.

Coherent states $|\alpha\rangle_0$ are eigenstates of the phonon annihilation operator a with complex eigenvalues α,

$$a|\alpha\rangle_0 = \alpha|\alpha\rangle_0, \quad \alpha \in C \tag{1.2.14}$$

and are usually labeled by Greek symbols. We have

$$b|0\rangle_\lambda = 0 \rightsquigarrow a|0\rangle_\lambda = -\lambda|0\rangle_\lambda \rightsquigarrow |0\rangle_\lambda \equiv X_\lambda|0\rangle_0 = |-\lambda\rangle_0. \tag{1.2.15}$$

The ground state of H_λ thus is a coherent state $|\alpha\rangle_0$ in the basis of the unshifted oscillator with $\alpha = -\lambda$.

Diagonalized System Hamiltonian $\mathcal{H}_S$

The diagonalized system Hamiltonian $\mathcal{H}_S$ with two electronic states, empty $|0\rangle_e$ and occupied $|1\rangle_e$, therefore has eigenstates

$$|0n\rangle \equiv |0\rangle_e \otimes |n\rangle_0, \quad |1n\rangle \equiv |1\rangle_e \otimes |n\rangle_\lambda. \tag{1.2.16}$$

1.3 The Polaron Transformation

The **polaron transformation** is a general method to treat problems with *linear* coupling between electrons and phonons, such as in our model $\mathcal{H}$, Eq. (1.2.1). We discuss the method first for our system Hamiltonian $\mathcal{H}_S$, Eq. (1.2.2), which, of course, will reproduce our previous results for the shifted oscillator.

1.3.1 System Hamiltonian

We introduce a unitary transformation for all operators $\hat{O}$, including the Hamiltonian,

$$\hat{O} \to \bar{O} \equiv e^S \hat{O} e^{-S}, \quad S \equiv n_d \lambda (a^\dagger - a). \tag{1.3.1}$$

The operator $U \equiv e^S$ is unitary because $U^{-1} = U^\dagger$, i.e. $UU^\dagger = U^\dagger U = 1$. Note that n_d in the definition of S is the electron number *operator* and not just a number (0 or 1) which is important when it comes to transforming d and $d^\dagger$ for the dot electrons.

For explicit calculations, one has to use the *nested commutator expansion* [1],

$$\bar{O} = O + [S, O] + \frac{1}{2!}[S,[S,O]] + \frac{1}{3!}[S,[S,[S,O]]] + ... \tag{1.3.2}$$

---

[1] The nested commutator expansion is proved by solving a first order differential equation for $f(x) \equiv e^{xS}\hat{O}e^{-xS}$, using a power series in x and comparing coefficients.

We first transform the electron number operator n_d,

$$\bar{n}_d = n_d + [S, n_d] + ... = n_d, \tag{1.3.3}$$

because S and n_d commute. This is not the case for the phonon annihilation operator a,

$$\begin{aligned} \bar{a} &= a + [S, a] + \frac{1}{2!}[S, [S, a]] + ... = a + n_d\lambda[a^\dagger - a, a] + ... \\ &= a - n_d\lambda, \end{aligned} \tag{1.3.4}$$

because $[a^\dagger, a] = -1$ is a scalar and all the higher commutators disappear. Correspondingly,

$$\begin{aligned} \bar{a}^\dagger &= a^\dagger + [S, a^\dagger] + \frac{1}{2!}[S, [S, a^\dagger]] + ... = a^\dagger + n_d\lambda[a^\dagger - a, a^\dagger] + ... \\ &= a^\dagger - n_d\lambda, \end{aligned} \tag{1.3.5}$$

as we expected by taking the canonical conjugate of $\bar{a}$.

Transforming now all operators individually, the polaron transformed $\mathcal{H}_S$ is

$$\begin{aligned} \bar{\mathcal{H}}_S &= e^S\mathcal{H}_S e^{-S} = \omega_0 e^S a^\dagger e^{-S} e^S a e^{-S} + \lambda\omega_0 e^S(a + a^\dagger)e^{-S} e^S n_d e^{-S} + \varepsilon e^S n_d e^{-S} \\ &= \omega_0 \bar{a}^\dagger \bar{a} + \lambda\omega_0(\bar{a} + \bar{a}^\dagger)\bar{n}_d + \varepsilon\bar{n}_d \\ &= \omega_0\left(\left(a^\dagger - n_d\lambda\right)\left(a - n_d\lambda\right)\right) + \lambda\omega_0(a - n_d\lambda + a^\dagger - n_d\lambda)n_d + \varepsilon n_d \\ &= \omega_0 a^\dagger a + \varepsilon n_d - \omega_0\lambda^2 n_d^2. \end{aligned} \tag{1.3.6}$$

The square of the number operator is just the number operator itself, $n_d^2 = n_d$: there is either one or no electron on the level (n_d thus is a projection operator that projects onto the number of electrons on the level). We can thus write

$$\bar{\mathcal{H}}_S = \omega_0 a^\dagger a + (\varepsilon - \omega_0\lambda^2)n_d. \tag{1.3.7}$$

The effect of the polaron transformation is thus twofold:

- the transformed Hamiltonian $\bar{\mathcal{H}}_S$ is diagonal in the (old, unshifted) phonon operators a and $a^\dagger$: the linear term with the coupling to n_d has been transformed away.
- the energy ε has been shifted into a lower energy $\varepsilon - \omega_0\lambda^2$ (the phonon frequency is always positive, $\omega_0 > 0$).

How do we now use the polaron transformation in oder to obtain the eigenvalues ϵ_n and eigenstates $|n\rangle_\lambda$ of $\mathcal{H}_S$? As $\bar{\mathcal{H}}_S$ is diagonal in the old phonon operators, one obviously has

$$\bar{\mathcal{H}}_S|n\rangle_0 = (n\omega_0 + \varepsilon - \omega_0\lambda^2)|n\rangle_0, \tag{1.3.8}$$

where $|n\rangle_0$ are the usual eigenstates of the phonon number operator $a^\dagger a$. This is, however, still in the polaron-transformed frame. We obtain the eigenstates $|n\rangle_\lambda$ of the original $\mathcal{H}_S$ by back-transforming: write the eigenvalue equation for vibrational states of the occupied level $n_d = 1$ as

$$\begin{aligned}\mathcal{H}_S|n\rangle_\lambda &= \epsilon_n|n\rangle_\lambda, \rightsquigarrow \bar{\mathcal{H}}_S e^S|n\rangle_\lambda = \epsilon_n e^S|n\rangle_\lambda \\ \rightsquigarrow \omega_0 a^\dagger a e^S|n\rangle_\lambda &= (\epsilon_n - \varepsilon + \omega_0\lambda^2)e^S|n\rangle_\lambda \qquad (1.3.9)\end{aligned}$$

Comparing with the usual, unshifted harmonic oscillator eigenvalue equation yields

$$e^S|n\rangle_\lambda = |n\rangle_0, \quad n\omega_0 = \epsilon_n - \varepsilon + \omega_0\lambda^2. \qquad (1.3.10)$$

The eigenvalues ϵ_n and eigenstates $|n\rangle_\lambda$ of $\mathcal{H}_S$ are therefore

$$|n\rangle_\lambda = e^{-S}|n\rangle_0 = e^{\lambda(a-a^\dagger)}|n\rangle_0, \quad \epsilon_n = n\omega_0 + \varepsilon - \omega_0\lambda^2. \qquad (1.3.11)$$

1.3.2 Total Hamiltonian

Electron transport through the system is introduced by connecting to left and right electron reservoirs in thermal equilibrium at chemical potential μ_L (μ_R) with positive source-drain voltage $V_{SD} \equiv \mu_L - \mu_R > 0$, inducing tunneling of electrons from the left to the right. We recall that the total Hamiltonian is $\mathcal{H} = \mathcal{H}_S + \mathcal{H}_V + \mathcal{H}_{\rm res}$, Eq. (1.2.1). We recall that the total Hamiltonian (system plus coupling to leads) is

$$\begin{aligned}\mathcal{H} &= \mathcal{H}_S + \mathcal{H}_V + \mathcal{H}_{\rm res}, \quad \mathcal{H}_{\rm res} \equiv= \sum_{k,\alpha=L/R} \varepsilon_{k,\alpha} c^\dagger_{k\alpha} c_{k\alpha} \qquad (1.3.12) \\ \mathcal{H}_V &= \sum_{k\alpha}(V_{k\alpha}c^\dagger_{k\alpha}\hat{s} + H.c.), \quad \hat{s} \equiv |0\rangle\langle 1|. \qquad (1.3.13)\end{aligned}$$

We have to transform $s = |0\rangle\langle 1|$, and using the commutator

$$[n_d, s] = |1\rangle\langle 1|0\rangle\langle 1| - |0\rangle\langle 1|1\rangle\langle 1| = -s, \qquad (1.3.14)$$

we obtain from the nested commutators with $S \equiv n_d\lambda(a^\dagger - a)$,

$$\begin{aligned}\bar{s} &\equiv e^S\hat{s}e^{-S} = s + [S, s] + \frac{1}{2!}[S,[S,s]] + ... \\ &= s - \lambda(a^\dagger - a)s + \frac{1}{2!}\left(\lambda(a^\dagger - a)\right)^2 s - ... = Xs \\ X &\equiv e^{\lambda(a-a^\dagger)} \qquad (1.3.15)\end{aligned}$$

The transformed Hamiltonian thus is

$$\bar{\mathcal{H}} = \omega_0 a^\dagger a + (\varepsilon - \omega_0\lambda^2)n_d + \sum_{k\alpha}(V_{k\alpha}c^\dagger_{k\alpha}\hat{s}X + H.c.) + \mathcal{H}_{\rm res}. \qquad (1.3.16)$$

We note that the electon reservoir Hamiltonian, $\mathcal{H}_{\rm res}$, is left invariant under the polaron transformation.

1.3.3 Polaron-transformed Master Equation

The Master equation is now derived in second order perturbation theory in the coupling to the leads. Performing the commutators and using the free time evolution of the electron reservoir operators, one finds

$$\begin{aligned}
\frac{d}{dt}\tilde{\rho}(t) &= -\sum_{k\alpha=L/R}\int_0^t dt' g_{k\alpha}(t-t')\left\{\tilde{s}(t)\tilde{s}^\dagger(t')\tilde{\rho}(t')-\tilde{s}(t')^\dagger\tilde{\rho}(t')\tilde{s}(t)\right\}\\
&- \sum_{k\alpha}\int_0^t dt'\bar{g}_{k\alpha}(t'-t)\left\{\tilde{s}^\dagger(t)\tilde{s}(t')\tilde{\rho}(t')-\tilde{s}(t')\tilde{\rho}(t')\tilde{s}^\dagger(t)\right\}\\
&- \sum_{k\alpha}\int_0^t dt' g_{k_\alpha}(t'-t)\left\{\tilde{\rho}(t')\tilde{s}(t')\tilde{s}^\dagger(t)-\tilde{s}^\dagger(t)\tilde{\rho}(t')\tilde{s}(t')\right\}\\
&- \sum_{k\alpha}\int_0^t dt'\bar{g}_{k\alpha}(t-t')\left\{\tilde{\rho}(t')\tilde{s}^\dagger(t')\tilde{s}(t)-\tilde{s}(t)\tilde{\rho}(t')\tilde{s}^\dagger(t')\right\}\\
g_{k\alpha}(\tau) &\equiv |V_{k\alpha}|^2 f^\alpha(\varepsilon_k)e^{i\varepsilon_k\tau},\quad \bar{g}_{k\alpha}(\tau)\equiv|V_{k\alpha}|^2[1-f^\alpha(\varepsilon_k)]e^{i\varepsilon_k\tau},
\end{aligned}\tag{1.3.17}$$

with the Fermi distributions $f^\alpha(\varepsilon_{k_i})\equiv \mathrm{Tr}_{\mathrm{res}}(R_0 c^\dagger_{k\alpha}c_{k\alpha})$. Here, the time evolution of the polaron-transformed s-operators is

$$\tilde{s}(t)\equiv e^{i\bar{\mathcal{H}}_S t}\bar{s}e^{-i\bar{\mathcal{H}}_S t}.\tag{1.3.18}$$

The sums over k can be written as integrals, introducing the tunneling density of states $\nu_\alpha(\varepsilon)$ in lead α,

$$\sum_k |V_{k\alpha}|^2 f^\alpha(\varepsilon_k)e^{i\varepsilon_k(t-t')}=\int_{-\infty}^{\infty}d\varepsilon\nu_\alpha(\varepsilon)f^\alpha(\varepsilon)e^{i\varepsilon(t-t')},\quad \nu_\alpha(\varepsilon)\equiv\sum_k|V_{k\alpha}|^2\delta(\varepsilon-\varepsilon_k).\tag{1.3.19}$$

The further calculation is now performed as follows:

1. Take matrix elements of Eq. (1.3.17) by ‘sandwiching’ as

   $$\langle 0,n|...|0,n'\rangle,\quad \langle 1,n|...|1,n'\rangle,\tag{1.3.20}$$

   where $|0n\rangle\equiv|0\rangle_e\otimes|n\rangle_0$ etc. as in Eq. (1.2.16). In particular, the phonon numbers n refer to the un-shifted harmonic oscillator.

   EXERCISE: Check that there are no terms $\langle 0,n|...|1,n'\rangle$, $\langle 1,n|...|0,n'\rangle$. This means that there are no coherences between occupied and un-occupied states.

2. Explicitly insert the time-dependence of the $\tilde{s}(t')$ etc.

3. Perform the *Markov approximation* (if required) in the interaction picture.

4. Transform back into the Schrödinger picture via

$$\begin{aligned}
\langle 0,n|\rho(t)|0,n'\rangle &= e^{i(\varepsilon_{0n'}-\varepsilon_{0n}t)}\langle 0,n|\tilde{\rho}(t)|0,n'\rangle && (1.3.21)\\
\frac{d}{dt}\langle 0,n|\rho(t)|0,n'\rangle &= i(\varepsilon_{0n'}-\varepsilon_{0n})\langle 0,n|\rho(t)|0,n'\rangle \\
&+ e^{i(\varepsilon_{0n'}-\varepsilon_{0n}t)}\frac{d}{dt}\langle 0,n|\tilde{\rho}(t)|0,n'\rangle . && (1.3.22)
\end{aligned}$$

5. Check that in all exponents the time-dependence is always via $t-t'$.

This derivation yields

$$\begin{aligned}
\left[\frac{d}{dt}-i(\varepsilon_{0n'}-\varepsilon_{0n})\right]\langle 0,n|\rho(t)|0,n'\rangle = -\sum_{mm'\alpha}\int_{-\infty}^{\infty}d\varepsilon\nu_\alpha(\varepsilon)\int_0^t dt' \times \\
f_\alpha(\varepsilon)\langle 0,m'|\rho(t)|0,n'\rangle\langle n|X|m\rangle\langle m|X^\dagger|m'\rangle e^{i(\varepsilon-\varepsilon_{1m}+\varepsilon_{0m'})(t-t')} \\
+\; f_\alpha(\varepsilon)\langle 0,n|\rho(t)|0,m\rangle\langle m|X|m'\rangle\langle m'|X^\dagger|n'\rangle e^{-i(\varepsilon-\varepsilon_{1m'}+\varepsilon_{0m})(t-t')} \\
-\; \bar{f}_\alpha(\varepsilon)\langle 1,m|\rho(t)|1,m'\rangle\langle n|X|m\rangle\langle m'|X^\dagger|n'\rangle e^{-i(\varepsilon-\varepsilon_{1m}+\varepsilon_{0n})(t-t')} \\
-\; \bar{f}_\alpha(\varepsilon)\langle 1,m|\rho(t)|1,m'\rangle\langle n|X|m\rangle\langle m'|X^\dagger|n'\rangle e^{i(\varepsilon-\varepsilon_{1m'}+\varepsilon_{0n'})(t-t')}
\end{aligned} \qquad (1.3.23)$$

and a corresponding equation for the $\langle 1,n|\rho(t)|1,n'\rangle$. The **Franck-Condon Factors**

$$\langle n|X|m\rangle \qquad (1.3.24)$$

etc. are determined by the overlap of the vibrational wave functions before and after tunneling of one electron. They strongly determine the electronic transportin our model, in particular if the electron-phonon coupling is strong which means $\lambda \sim 1$ or larger.

1.4 Franck-Condon Factors

1.4.1 Born-Oppenheimer Approximation in Molecular Physics

(This is from my lectures notes ‘Quantum Mechanics of Atoms and Molecules’).

Molecules are system consisting of electrons and nuclei. This definition covers the full range from rather simple molecules like H_2 up to extremely complex situations with billions of nuclei, or in principle even solids or fluids although one usually thinks of something like a microscopic object. The question, of course, is what microscopic really means. In principle, one could have molecules with macroscopic large numbers (like 10^{23}) of electrons and nuclei. Would these behave as quantum or as classical objects?

Model Hamiltonian

We start from a Hamiltonian describing a system composed of two sub-systems, electrons (e) and nuclei (n)

$$\mathcal{H} = \mathcal{H}_{\rm e} + \mathcal{H}_{\rm n} + \mathcal{H}_{\rm en}, \tag{1.4.1}$$

where $\mathcal{H}_{\rm en}$ is the interaction between the two systems. Note that the splitting of the Hamiltonian $\mathcal{H}$ is not unique: for example, $\mathcal{H}_{\rm n}$ could just be the kinetic energy of the nuclei with their mutual interaction potential included into $\mathcal{H}_{\rm en}$ (as in the BO approximation).

The set-up $\mathcal{H} = \mathcal{H}_{\rm e}+\mathcal{H}_{\rm n}+\mathcal{H}_{\rm en}$ is quite general and typical for so-called 'system-bath' theories where one would say the electrons are the 'system' and the nuclei are the 'bath' (or vice versa!). In the theory of molecules, however, things are a little bit more complicated as there is a back-action of from the electrons on the nuclei. This back-action is due to the electronic charge density acting as a potential for the nuclei.

There is no *a priori* reason why the nuclei and the electronic system should not be treated on equal footing. However, the theory has a small parameter

$$\kappa = \left(\frac{m}{M}\right)^{\frac{1}{4}} \tag{1.4.2}$$

given by the ratio of electron mass m and a typical nuclear mass $M \gg m$, and the exponent $1/4$ is introduced for convenience in the perturbation theory used by Born and Oppenheimer in their original paper. The smallness of this parameter makes it possible to use an approximation which is called the **Born-Oppenheimer approximation**.

We assume there is a position representation, where $q \equiv \{\mathbf{x_1}, ..., \mathbf{x_N}\}$ represents the positons of all electrons, $X \equiv \{\mathbf{X_1}, ..., \mathbf{X_N}\}$ the positions of all nuclei, and correspondingly for the momenta p and P,

$$\mathcal{H} = \mathcal{H}(q,p;X,P) = \mathcal{H}_{\rm e}(q,p) + \mathcal{H}_{\rm n}(X,P) + \mathcal{H}_{\rm en}(q,X). \tag{1.4.3}$$

Spin is not considered here. Also note that the interaction only depends on (q, X) and not on the momenta.

The Born-Oppenheimer Approximation

This is the central aproximation used in many calculations. We now try to attack the Schrödinger equation $\mathcal{H}\Psi = \mathcal{E}\Psi$ for the total system (electron plus nuclei).

A first guess to solve the stationary Schrödinger equation $\mathcal{H}\Psi = \mathcal{E}\Psi$ for the total system would be a separation *ansatz*

$$\begin{aligned} \mathcal{H}(q,p;X,P)\Psi(q,X) &= \mathcal{E}\Psi(q,X) \\ \Psi(q,X) &= \psi_e(q)\phi_n(X) \quad \text{unsuccessful}, \end{aligned} \tag{1.4.4}$$

which does not work because the interaction $\mathcal{H}_{\rm en}(q,X)$ depends on both q *and* X.

As $\mathcal{H}_{\rm en}(q,X)$ depends on the positions of the nuclei X, let us try an *ansatz*

$$\Psi(q,X) \;=\; \psi_e(q,X)\phi_n(X) \quad \text{successful} \tag{1.4.5}$$

where now the electronic part depends on the nuclear coordinates X as well. This looks unsymmetric: why shouldn't one have $\Psi(q,X)=\psi_e(q,X)\phi_n(q,X)$? First, there *is* an asymmetry in the problem in the form of $M \gg m$, and $\Psi(q,X) = \psi_e(q,X)\phi_n(q,X)$ is no more better than $\Psi(q,X)$ in the first place.

The idea with writing $\Psi(q,X)=\psi_e(q,X)\phi_n(X)$ is that the electronic part $\psi_e(q,X)$ already solves part of the problem, i.e.

$$\left[\mathcal{H}_{\rm e}(q,p)+\mathcal{H}_{\rm en}(q,X)\right]\psi_e(q,X)=E(X)\psi_e(q,X), \tag{1.4.6}$$

an equation in which X, of course, appears as an *external classical parameter* that commutes with all other variables. Consequently, the eigenvalue $E(X)$ has to depend on X. We thus obtain

$$\begin{aligned}\mathcal{H}\psi_e\phi_n &\equiv \left[\mathcal{H}_{\rm e}+\mathcal{H}_{\rm n}+\mathcal{H}_{\rm en}\right]\psi_e\phi_n\\ &= \left[\mathcal{H}_{\rm n}+E(X)\right]\psi_e\phi_n \quad (?) = \mathcal{E}\psi_e\phi_n\end{aligned} \tag{1.4.7}$$

where the last questionmark indicated what we would like to have! Since $\mathcal{H}_{\rm n}$ and $E(X)$ depend on the nuclear coordinates only, one would like to use an equation like

$$\left[\mathcal{H}_{\rm n}+E(X)\right]\phi_n(X)=\mathcal{E}\phi_n(X), \tag{1.4.8}$$

because then we would have achieved our goal. However, the operator $\mathcal{H}_{\rm n}$ contains the nuclear momenta P which operate on the X in $\psi_e(q,X)$, i.e.

$$\begin{aligned}\mathcal{H}\psi_e\phi_n &= \psi_e\left[\mathcal{H}_{\rm n}+E(X)\right]\phi_n+\underline{\left[\mathcal{H}_{\rm n}\psi_e\phi_n-\psi_e\mathcal{H}_{\rm n}\phi_n\right]}\\ &= \mathcal{E}\psi_e\phi_n+\underline{\left[\mathcal{H}_{\rm n}\psi_e\phi_n-\psi_e\mathcal{H}_{\rm n}\phi_n\right]}.\end{aligned} \tag{1.4.9}$$

This shows that we are almost there if it wasn't for the underlined term. One now tries to find arguments why this term can be neglected. If it can be neglected, then we have achieved the full solution of the Schrödinger equation by the two separate equations

$$\begin{aligned}\left[\mathcal{H}_{\rm e}(q,p)+\mathcal{H}_{\rm en}(q,X)\right]\psi_e(q,X) &= E(X)\psi_e(q,X) \quad \text{electronic part}\\ \left[\mathcal{H}_{\rm n}+E(X)\right]\phi_n(X) &= \mathcal{E}\phi_n(X) \quad \text{nuclear part.}\end{aligned} \tag{1.4.10}$$

These two equations Eq. (1.4.10) are the central equations of the **Born-Oppenheimer approximation**. Even without solving them, some quite interesting observations can already be made:

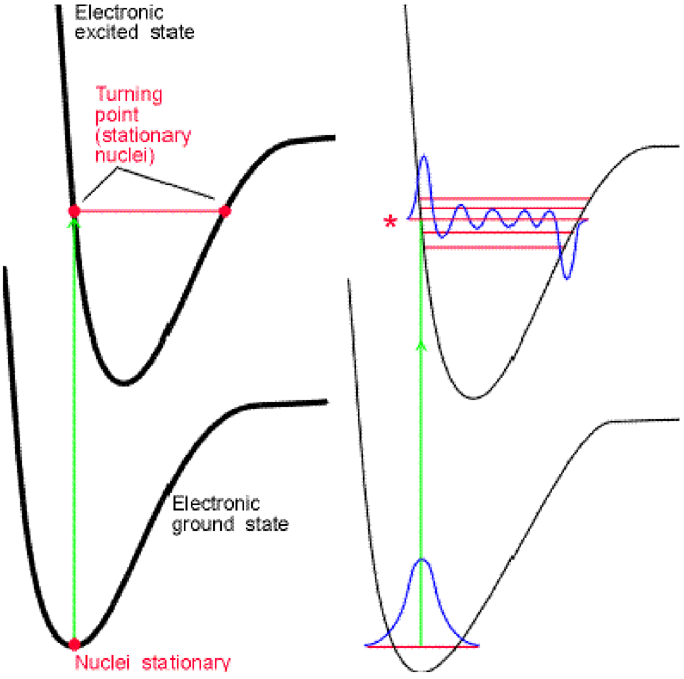

Figure 1.1: Franck-Condon-Principle. **Left:** Classical picture, **right:** quantum-mechanical picture. From Prof. Ed Castner's lecture http://rutchem.rutgers.edu/.

- The electronic part is calculated as if the nuclei were at fixed positions X ('clamped nuclei').
- The eigenvalue of the energy of the electronic part serves as a *potential* energy for the nuclei in the nuclear part of the equations.

The Franck-Condon Principle

Here, a good description is in Atkins/Friedman ch. 11.4.

We consider a transition $\alpha \to \alpha'$ between two molecular states due to, e.g., an optical excitation. For simplicity, we leave out the molecular rotations here and just discuss electronic and vibrational transitions. In a classical picture (with respect to the large mass nuclear motion), one considers the two effective potentials $U_\alpha(r)$ and $U_{\alpha'}(r)$ acting on the nuclei as given functions. One then argues that the electronic transition occurs so fast that the nuclear system has no time to react: before and after the transition, the nuclear coordinate X is the same. This, however, means that the distance $|x'| \equiv |X - r_{\alpha'}|$ from the equilibrium position $r_{\alpha'}$ after the transition and the distance $|x| \equiv |X - r_\alpha|$ from the equilibrium position r_α before the transition are not the same: when the nuclei are in equilibrium before the transition ($X = r_\alpha, x = 0$), their new coordinate x' *relative to the new equilibrium* $r_{\alpha'}$ is $x' \equiv X - r_{\alpha'} = r_\alpha - r_{\alpha'} \neq 0$ after the transition.

The optical transition depends on the total dipole moment operator which is a sum of electronic and nuclear dipole moment,

$$\mathbf{d} = -e \sum_i \mathbf{q}_i + e \sum_s Z_s \mathbf{X}_s = \mathbf{d}_e + \mathbf{d}_\mathrm{n}. \tag{1.4.11}$$

The transition matrix element in Born-Oppenheimer approximation is ($\alpha \neq \alpha'$)

$$\begin{aligned}
\langle \alpha' v' | \mathbf{d}_e + \mathbf{d}_\mathrm{n} | \alpha v \rangle &= \int dq dX \psi^*_{\alpha'}(qX) \phi^*_{\alpha',v'}(X) (\mathbf{d}_e + \mathbf{d}_\mathrm{n}) \phi_{\alpha,v}(X) \psi_\alpha(qX) \\
&= \int dX \phi^*_{\alpha',v'}(X) \left[\int dq \psi^*_{\alpha'}(qX) \mathbf{d}_e \psi_\alpha(qX) \right] \phi_{\alpha,v}(X) \\
&+ \int dX \phi^*_{\alpha',v'}(X) \phi_{\alpha,v}(X) \mathbf{d}_\mathrm{n} \int dq \psi^*_{\alpha'}(qX) \psi_\alpha(qX) \\
&= \int dX \phi^*_{\alpha',v'}(X) \left[\int dq \psi^*_{\alpha'}(qX) \mathbf{d}_e \psi_\alpha(qX) \right] \phi_{\alpha,v}(X) + 0 \\
&\approx \langle \alpha' | \mathbf{d}_e | \alpha \rangle S(v, v'), \quad S(v, v') \equiv \langle v' | v \rangle.
\end{aligned} \tag{1.4.12}$$

Here it was assumed that the integral

$$\int dq \psi^*_{\alpha'}(qX) \mathbf{d}_e \psi_\alpha(qX) \approx \langle \alpha' | \mathbf{d}_e | \alpha \rangle \tag{1.4.13}$$

does not depend on the nuclear coordinates X.

The transition between two electronic levels α and α' is therefore determined by the dipole matrix element $\langle \alpha' | \mathbf{d}_e | \alpha \rangle$ and the **Franck-Condon factors** $S(v, v')$, which are the overlap integrals of the corresponding vibronic states. As these states belong to different electronic states α and α', the overlaps are not zero, and there is also no selection rule for Δv.

1.4.2 Example: Linear Oscillator Coupling

In this model, the Franck-Condon factors can be calculated analytically: they are given by the phonon number matrix elements of the displacement operator

$$D(\alpha) \equiv e^{\alpha(a^\dagger - a)} \tag{1.4.14}$$

and can be obtained using $|n\rangle \equiv (1/\sqrt{n!})(a^\dagger)^n |0\rangle$ and

$$\langle m | D(\alpha) | n \rangle = e^{\frac{1}{2}|\alpha|^2} \frac{1}{\sqrt{n! m!}} \frac{\partial^{n+m}}{\partial z_1^m \partial z_2^n} \langle 0 | e^{(z_1 - \alpha^*) a} e^{(z_2 + \alpha) a^\dagger} | 0 \rangle \Big|_{z_1 = z_2 = 0}.$$

With $\langle 0|e^{(z_1-\alpha^*)a}e^{(z_2+\alpha)a^\dagger}|0\rangle = e^{(z_1-\alpha^*)(z_2+\alpha)}$, in the case $m \geq n$ the differentiation yields

$$\langle m|D(\alpha)|n\rangle = e^{\frac{1}{2}|\alpha|^2}\frac{1}{\sqrt{n!m!}}\frac{\partial^n}{\partial z_2^n}(z_2+\alpha)^m e^{-(z_2+\alpha)\alpha^*}\bigg|_{z_2+\alpha}. \quad (1.4.15)$$

Comparison with the generating function of the Laguerre polynomials [1] yields

$$\begin{aligned}\langle m|D(\alpha)|n\rangle &= \sqrt{\frac{n!}{m!}}\alpha^{m-n}e^{-\frac{1}{2}|\alpha|^2}L_n^{m-n}\left(|\alpha|^2\right) & (1.4.16)\\ &= \langle m|D^\dagger(\alpha)|n\rangle^* = (-1)^{m-n}\langle m|D(\alpha)|n\rangle^*. & (1.4.17)\end{aligned}$$

A corresponding expression can be derived for $n \geq m$.

1.4.3 Franck-Condon Factors in Electron Scattering and Tunneling

We consider a single electron in one dimension,

$$\mathcal{H} = \frac{p^2}{2m} + \lambda(x)\omega_0(a+a^\dagger) + \omega_0 a^\dagger a. \quad (1.4.18)$$

Step change, $\lambda(x) = \theta(x)\lambda, \quad \lambda > 0$

In this case, the wave function for scattering states at energy $E > 0$ can be written as

$$\begin{aligned}\Psi(x\leq 0) &= \sum_{n=0}^{\infty}\left(a_n e^{ik_n x} + b_n e^{-ik_n x}\right)|n\rangle_0\\ \Psi(x\geq 0) &= \sum_{n=0}^{\infty} t_n e^{ik'_n x}|n\rangle_\lambda & (1.4.19)\end{aligned}$$

with unshifted oscillator states $|n\rangle_0$ in the expansion on the right side and shifted oscillator states $|n\rangle_\lambda$ in the expansion on the left side of the step. Continuity of $\Psi(x)$ and $\Psi'(x)$ at $x = 0$ yields two equations

$$\begin{aligned}a_m + b_m &= \sum_{n=0}^{\infty} t_n\langle m|n\rangle_\lambda\\ k_m(a_m - b_m) &= \sum_{n=0}^{\infty} k'_n t_n\langle m|n\rangle_\lambda. & (1.4.20)\end{aligned}$$

We immediately recognize the appearance of the Franck-Condon Factors $\langle m|n\rangle_\lambda$ that describe the sudden change of the oscillator potential when the electron moves across the step.

Adiabatic change of $\lambda(x)$

In this opposite case, $\lambda(x)$ changes very slowly as a function of x: let $E > 0$ be the energy of a total scattering state (electron coming from the left). Then, the corresponding electron momentum is

$$p = \sqrt{2mE}, \tag{1.4.21}$$

and we write the time of flight t_f through a typical distance $\Delta x = \lambda'(x)/\lambda(x)$ over which the coupling potential $\lambda(x)$ varies as $t_f = m\Delta x/p$. Adiabaticity then means that the time of flight t_f is large compared with $1/\omega_0$,

$$\begin{aligned} \frac{m\omega_0}{\sqrt{2mE}} \frac{\lambda'(x)}{\lambda(x)} &\gg 1 \\ \omega_0 &\gg \sqrt{\frac{2E}{m\Delta x^2}} \end{aligned} \tag{1.4.22}$$

Replacing E by the minimum total energy which is the oscillator ground state energy $\frac{1}{2}\hbar\omega_0$ leads to

$$\frac{1}{2}\hbar\omega_0 \ll \frac{1}{2}m\omega_0^2 \Delta x^2 \tag{1.4.23}$$

as a condition for the adiabatic situation.

The adiabatic case is no longer simply describe by Franck-Condon factors. In contrast, the step change discussed above means $\Delta x = 0$ across the step and is thus the opposite of the adiabatic situation Eq. (1.4.22).

1.5 Franck-Condon Blockades and Noise for the $U = \infty$-Anderson-Holstein Model

1.5.1 Rate Equation Approximation

The Rate Equation Approximation consists in neglecting all non-diagonal elements of the reduced system density operator. We thus replace

$$\langle 0, n|\rho(t)|0, n'\rangle \to \delta_{nn'}\langle 0, n|\rho(t)|0, n\rangle \tag{1.5.1}$$

in all terms in the Master equation. The validity or otherwise of such an approximation is in general hard to check - unless one directly compares results from a Master Equation and a Rate Equation calculation for a given model. Usually, one argues that for certain types of calculations off-diagonal elements might be small and may thus be neglected. Using the Rate Equation Approximation in the

Master Equation of the small Polaron model, we find a set of differential equations for the *occupation probabilities*

$$P_{0,q}(t) \equiv \langle 0,q|\rho(t)|0,q\rangle, \quad P_{1,q}(t) \equiv \langle 1,q|\rho(t)|1,q\rangle, \tag{1.5.2}$$

where the label q is used here instead of n for the sake of a unified notation when comparing with recent results in the literature. The Rate Equations read

$$\begin{aligned}\dot{P}_{0,q} &= -\sum_{q'}\left[P_{0,q}\Gamma^{0\to 1}_{q\to q'} - P_{1,q'}\Gamma^{1\to 0}_{q'\to q}\right] & (1.5.3)\\ \dot{P}_{1,q} &= -\sum_{q'}\left[P_{1,q}\Gamma^{1\to 0}_{q\to q'} - P_{0,q'}\Gamma^{0\to 1}_{q'\to q}\right], & (1.5.4)\end{aligned}$$

where the transitions rates $\Gamma^{0\to 1}_{q\to q'}$ are defined as

$$\begin{aligned}\Gamma^{0\to 1}_{q\to q'} &= 2\sum_{\alpha=L,R}|\langle q|X|q'\rangle|^2\gamma_\alpha\left[\tilde{\varepsilon}+\omega_0(q'-q)\right] & (1.5.5)\\ \Gamma^{1\to 0}_{q'\to q} &= 2\sum_{\alpha=L,R}|\langle q|X|q'\rangle|^2\bar{\gamma}_\alpha\left[\omega_0(q'-q)\right] & (1.5.6)\\ \gamma_\alpha(\varepsilon) &\equiv \pi\nu_\alpha(\varepsilon)f_\alpha(\varepsilon), \quad \bar{\gamma}_\alpha(\varepsilon)\equiv\pi\nu_\alpha(\varepsilon)[1-f_\alpha(\varepsilon)]. & (1.5.7)\end{aligned}$$

The terms in Eq.(1.5.3) can be easily interpreted as follows: consider the level in the ‘empty’ state $0,q$ (no electron, phonon state q). This state changes by

– tunneling of an electron into the molecule at a rate $\Gamma^{0\to 1}_{q\to q'}$, leaving the molecule in vibrational state q'. The energy difference

$$E_{\text{final}} - E_{\text{initial}} = \varepsilon_{1q'} - \varepsilon_{0q} = \tilde{\varepsilon} + \omega_0(q'-q) \tag{1.5.8}$$

has to be provided by the leads: before tunneling onto the molecule, the electron must therefore have had the single particle energy $E_{\text{final}} - E_{\text{initial}}$ below the Fermi surface, which is why the rate is proportional to the occupation f_α of the leads from which the electron tunnels. Energy conservation requires

$$f_\alpha(E_{\text{final}} - E_{\text{initial}}) = f_\alpha\left(\tilde{\varepsilon} + \omega_0(q'-q)\right). \tag{1.5.9}$$

These processes lead to a decrease of the probability for the level being empty.

– tunneling of an electron from the molecule in state $1,q'$ into the lead at a rate $\Gamma^{0\to 1}_{q'\to q}$, leaving the molecule in vibrational state q and thus increasing $P_{0,q}$. The remaining energy, as given by the energy difference

$$E_{\text{initial}} - E_{\text{final}} = \varepsilon_{1q'} - \varepsilon_{0q} = \tilde{\varepsilon} + \omega_0(q'-q), \tag{1.5.10}$$

is now provided to the leads in the form of an additional electron with single particle energy $E_{\mathrm{initial}} - E_{\mathrm{final}}$ above the Fermi surface, which is why this rate is proportional to the Pauli-block factor

$$1 - f_\alpha(E_{\mathrm{initial}} - E_{\mathrm{final}}) = 1 - f_\alpha\left(\tilde{\varepsilon} + \omega_0(q' - q)\right). \tag{1.5.11}$$

Note that in both cases the argument of the Fermi function is the same. Furthermore, the tunneling density of states ν_α gives the number of possible single-particle states in the lead α with these energies. Finally, the squares of the Frank-Condon factors $|\langle q|X|q'\rangle|^2$ enter into all the transition rates: they describe the overlap of the vibrational wave functions according to the Frank-Condon principle.

1.5.2 Current and Noise

A typical current-voltage characteristic of the small polaron model with $\varepsilon = 0$ is shown in Fig. 1.5.2 a), which we took from the paper by Koch and v. Oppen [2]. For intermediate coupling strength $\lambda = 1$, the current increases in steps $\hbar\omega_0$ when the transport window

$$\mu_L = V/2 > \mu_R = -V/2 \tag{1.5.12}$$

is opened by increasing the source-drain (bias) voltage V across the molecule. For larger coupling strength $\lambda = 4$, the current is strongly suppressed at small V. This is due to the exponential suppression of the Frank-Condon factors $|\langle q|X|q'\rangle|^2$ at large λ (shown as two-dimensional 'histograms' in Fig. 1.5.2 b) which means that only processes with a significant energy difference $\omega_0(q' - q)$ contribute to transport, but at small V these are simply not allowed by energy conservation which therefore leads to a blockade of the current, the *Frank-Condon blockade.*

Koch and v. Oppen found that Monte-Carlo (quantum trajectory) calculations of the time-dependent rate equation Eq. (1.5.3) reveal deep insight into the transport process of the Anderson-Holstein model at strong coupling $\lambda = 4$. At intermediate voltage bias V, the transport is strongly suppressed by the Frank-Condon factors which leads to long periods where no electrons pass through the molecule which remain in, say, state $q = 0$. At large λ, the Frank-Condon factors exponentially grow with q for transitions with $0 \to q$. These rare transitions then trigger a chain of further transitions to still larger phonon numbers q, leading to an avalanche-type passage of a large number of electrons through the molecule in a very short space of time. These avalances are characterised by a hierarchical structure, i.e. when magnifying them as a function of time they display a similar structure on that new time-scale, again with long waiting times interrupted by 'second generation' avalanches, and so on. This is shown in Fig.1.5.2.

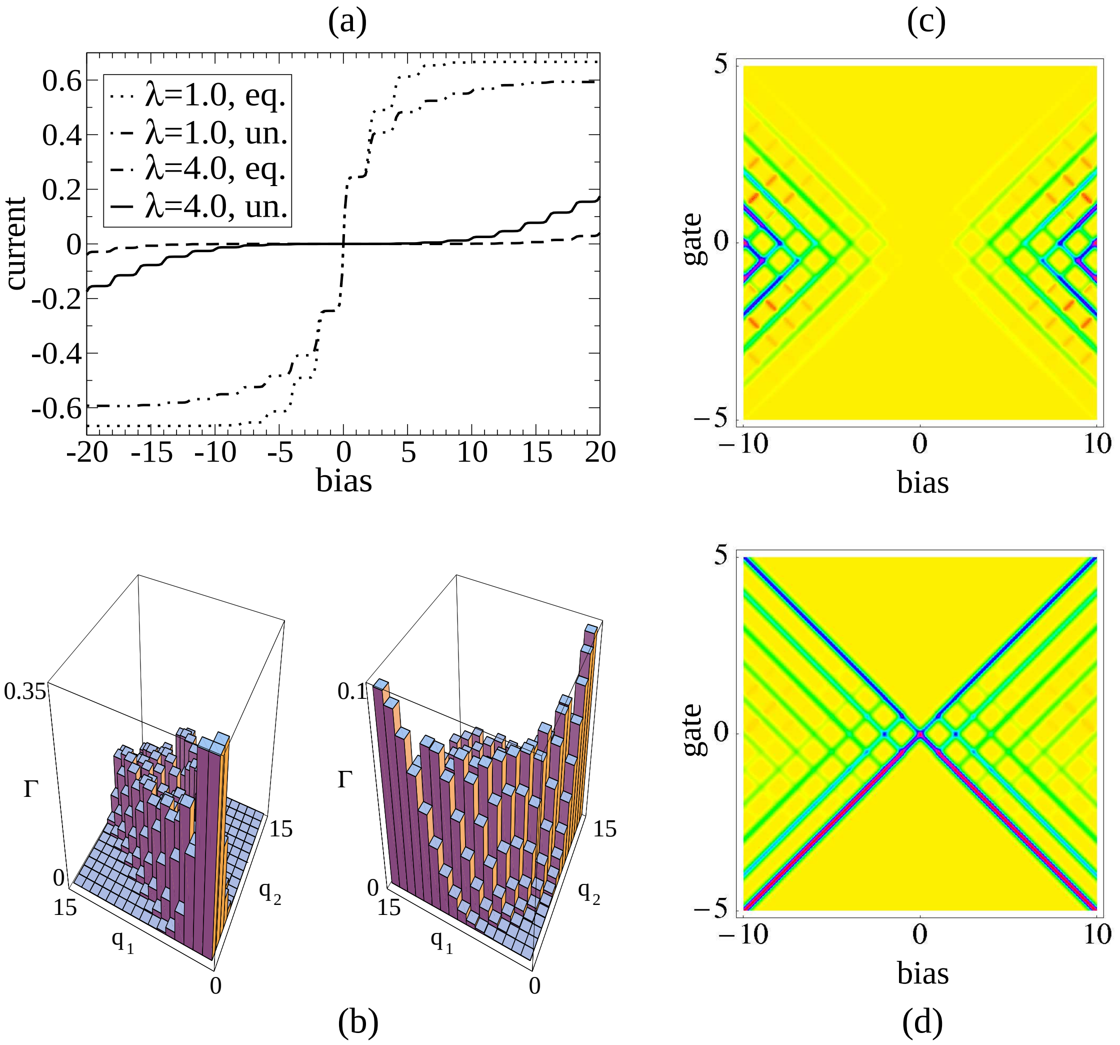

Figure 1.2: a) I-V curve for infinite-U Anderson-Holstein model at $\lambda = 1$ and $\lambda = 4$; b) Frank-Condon factors $|\langle q|X|q'\rangle|^2$ for $\lambda = 1$ (left) and $\lambda = 4$ (right); c) differential dI/dV plot at $\lambda = 4$ and d) at $\lambda = 1$. From Koch, v. Oppen, Phys. Rev. Lett. **94** 206804 (2005).

1.6 Nonlinear Electron-Phonon Coupling

We now discuss the case that is quite opposite to the linear electron-phonon coupling discussed so far. The material in this section is discussed in detail in a Diploma Thesis (Hannes Huebener, University of Hamburg 2007, unpublished).

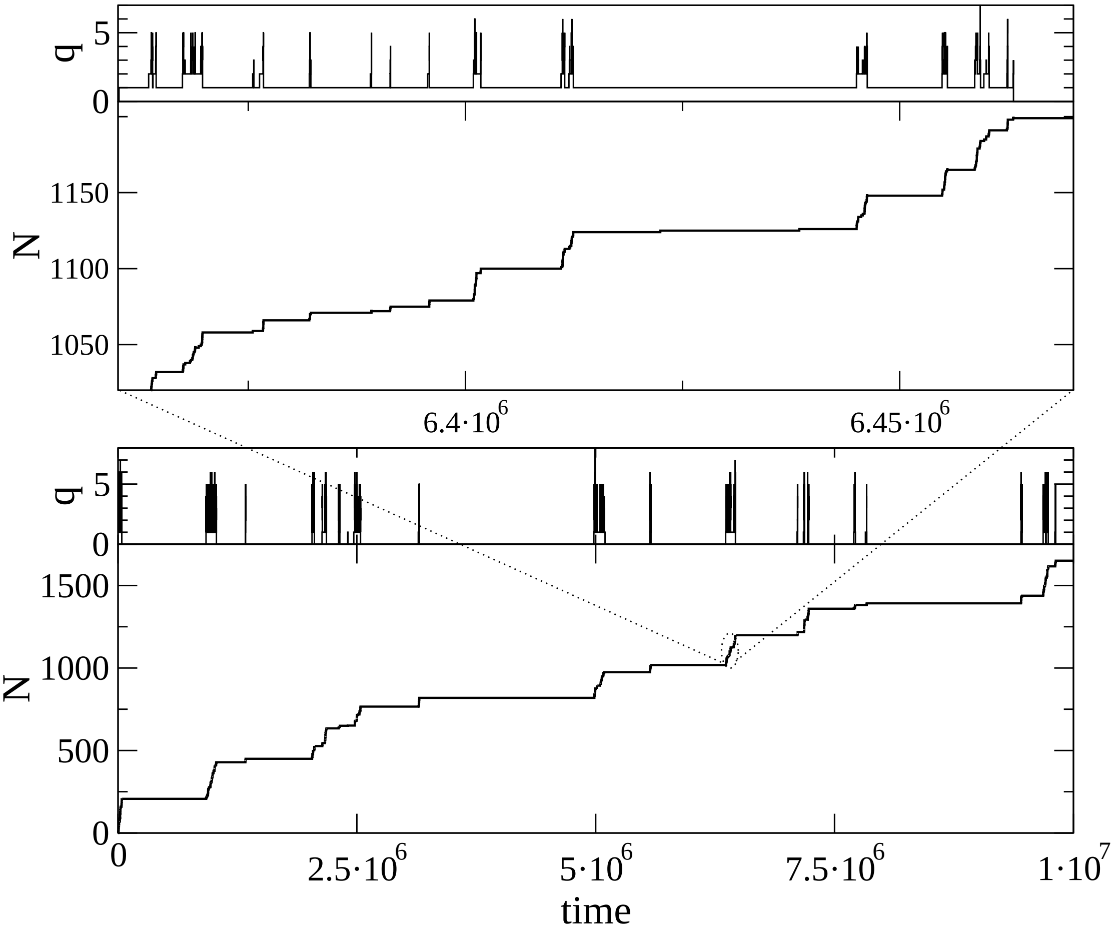

Figure 1.3: Avalanche type of transport for large $\lambda = 4$: The number of electrons $N(t)$ having passed through the molecule, and the phonon number $q(t)$ have a self-similar structure as a function of time t. Parameters are $T = 0.05\omega_0$ and $V = 3\omega_0$. From Koch, v. Oppen; Phys. Rev. Lett. **94**, 206804 (2005).

1.6.1 Model Hamiltonian

Our model system is a resonator or a molecule that can be charged and un-charged by tunneling of single electrons. We assume that the resonator oscillates in x-direction with harmonic oscillator frequency ω_0 and mean square displacement l_0 at zero temperature in the uncharged state. Charging with one additional electron leads to a Coulomb attraction towards a nearby metallic surface due to the image charge at distance $2a$ from the (uncharged) resonator equilibrium position, cf. Fig.1.4. We assume strong electronic Coulomb blockade and thus two electronic states ($|0\rangle$, 'empty' and $|1\rangle$, occupied), leading to the effective Hamiltonian of the

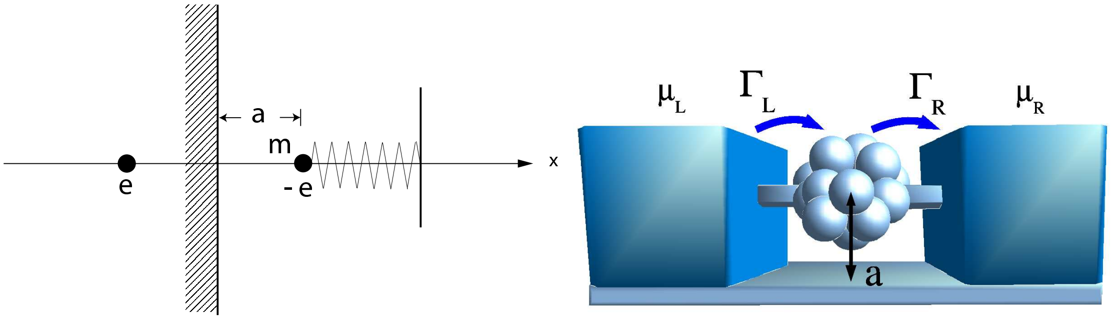

Figure 1.4: (Left) Oscillator near a conductive surface with image charge effect. (Right) single electrons (de)charging the dot at rates $\Gamma_L(\Gamma_R)$ lead to a switching between a harmonic resonator potential (oscillator length l_0) and a non-linear potential due to the Coulomb attraction of the charged resonator towards the surface. From Huebener, Brandes; preprint (cond-mat).

dot-resonator

$$\mathcal{H}_S \equiv \frac{\mathbf{p}^2}{2M} + \frac{1}{2}M\omega_0^2(\mathbf{a}-\mathbf{r})^2 - d^\dagger d\ \frac{e^2}{4\pi\epsilon_0 2\mathbf{r}\hat{\mathbf{u}}}, \tag{1.6.1}$$

where $M \equiv \hbar/l_0^2\omega_0$ is the effective oscillator mass of the resonator, $\hat{\mathbf{u}}$ the unit vector from the dot to the metallic surface, and $d^\dagger$ the creation operator of an electron on the dot, where for simplicity we disregard the electron's spin degree of freedom.

1.6.2 Vibrational Eigenstates

These have to be calculated by an exact diagonalization of $H_{\rm dot}$. In the three-dimensional problem, the resonator motion in x-direction decouples from the motion perpendicular to the x-axis for both charged and uncharged states, thus leaving us with an effectively one-dimensional problem: the uncharged vibrational states $|0,n\rangle$ simply are harmonic oscillator eigenstates with respect to the equilibrium position a. On the other hand, the charged states $|1,n\rangle$ are obtained by expansion into the eigenbasis of $l=0$ hydrogen atom eigenfunctions $\psi_n(x) = \sqrt{\frac{(n-1)!}{2n(n!)}}\left(\frac{2\epsilon}{n}\right)^{\frac{3}{2}} e^{-\frac{\epsilon}{n}x} x L^1_{n-1}\left(\frac{2\epsilon}{n}x\right)$ and subsequent numerical diagonalization. Here, x is measured from the metallic surface in units of a.

The system Hamiltonian thus can be written as

$$\mathcal{H}_S = \sum_{i=0,1}\sum_n \varepsilon_{i,n}|in\rangle\langle in|, \quad |i,n\rangle \equiv |i\rangle_e \otimes |n\rangle_i, \tag{1.6.2}$$

where $|n\rangle_0$ are the harmonic oscillator eigenstates and $|n\rangle_1$ are the vibrational eigenstates for the nonlinear potential $V(x)$ in which the charged oscillator moves, cf. Fig. 1.4.

The model has two dimensionless parameters,

$$\Omega \equiv \frac{M\omega_0}{\hbar} a^2 = \frac{a^2}{l_0^2}, \quad \epsilon \equiv \frac{e^2 M a}{8\hbar^2 \pi \varepsilon_0} = \Omega \frac{E_a}{\hbar\omega_0}, \tag{1.6.3}$$

where Ω determines the distance from the wall relative to the harmonic oscillator (zero-point fluctuation) length scale l_0, and ϵ is given by Ω times the typical Coulomb (charge - image charge) energy,

$$E_a \equiv \frac{e^2}{4\pi\varepsilon_0 2a}, \tag{1.6.4}$$

relative to the harmonic oscillator phonon energy $\hbar\omega_0$.

An important feature of the corresponding spectrum of the energy eigenvalues $\varepsilon_{\nu n}$ for $\nu = 1$ is the appearance of an avoided level crossing (Fig. 1.5(a) inset near $\Omega = 13.4$). This can be traced back to the effective double-well structure of $V(x)$ for coupling strengths $\epsilon > 9$. In this regime, the charged oscillator can be approximated by a two-level system at low energies, and one thus expects *quantum coherent behavior* due to tunneling between two states approximately localized around $x = a$ and $x = 0$ (i.e. near the surface). This vibrational tunneling can be made visible by electronic transport through the resonator, which requires the use of the full Master equations (and not the rate equations).

1.6.3 Coherences and Master Equations

As before, electrons jump off and onto the system according to

$$\mathcal{H}_V = \sum_{k\alpha = L/R} (V_{k\alpha} c_{k\alpha}^\dagger \hat{s} + H.c.), \quad \hat{s} \equiv |0\rangle\langle 1|. \tag{1.6.5}$$

There is no dependence on the vibrational degree of freedom at this stage! This comes in at the point where we formulate the Master equation. As before, we use our general expression Eq. (1.3.17) and the procedure outlines thereafter: take matrix elements of Eq. (1.3.17) by ‘sandwiching’ with the exact eigenstates of $\mathcal{H}_S$, insert the time-dependence of the $\tilde{s}(t')$ etc., perform the Markov approximation in the interaction picture and transform back into the Schrödinger picture. The only difference is that now we do not use a polaron transformation but rather work with the exact eigenstates of the system Hamiltonian $\mathcal{H}_S$. The result of this derivation

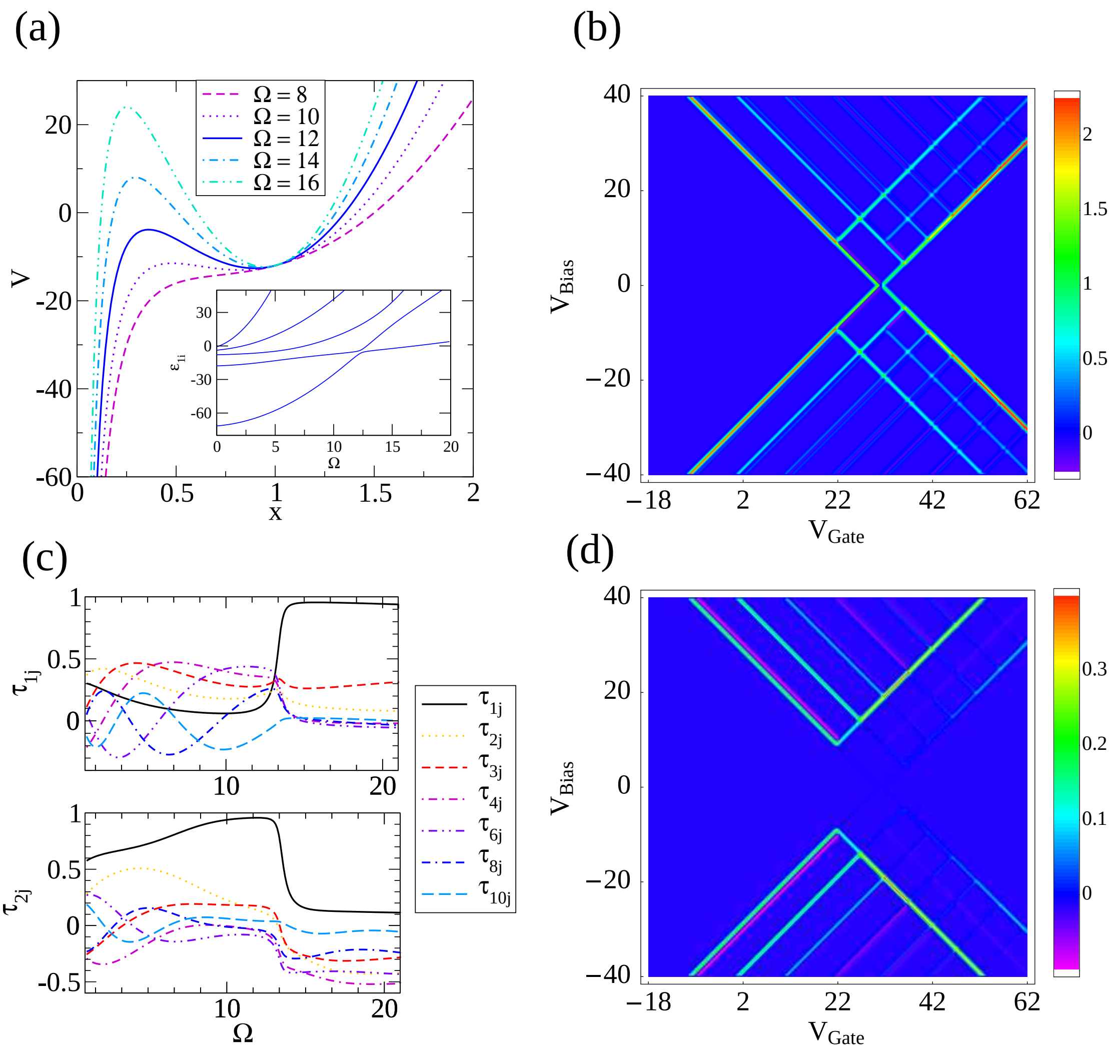

Figure 1.5: (color online). **(a)** Potential of an oscillator with image charge effect depending on the oscillator frequency Ω and the eigenvalue spectrum of the correspondong Hamiltonian (for $\epsilon = 12$) (inset). Level anti-crossing occurs at $\Omega = 13.4$. **(b)** Franck-Condon overlaps of the eigenfunctions of the charged and uncharged oscillator as a function of Ω. There are two different regimes before and after the anti-crossing point. **(c)** dI/dV as a function of gate and bias voltage for $\epsilon = 12$ and $\Omega = 11$ without the effect of the Franck-Condon factors ($\tau_{ij} = 1$) showing the usual conductance diamonds. **(d)** As (c) but with Franck-Condon factors: Current is surpressed for low bias and cannot be restored by changing the gate (Franck-Condon blockade). Negative differential conductance occurs as violet lines in the transport spectrum (c.f color scale)

yields

$$\begin{aligned}\left[\frac{d}{dt} - i(\varepsilon_{0n'} - \varepsilon_{0n})\right] \langle 0,n|\rho(t)|0,n'\rangle = -\sum_{mm'\alpha}\int_{-\infty}^{\infty} d\varepsilon\nu_\alpha(\varepsilon)\int_0^t dt' \times \\
& f_\alpha(\varepsilon)\langle 0,m'|\rho(t)|0,n'\rangle\langle 0,n|1,m\rangle\langle 1,m|0,m'\rangle e^{i(\varepsilon-\varepsilon_{1m}+\varepsilon_{0m'})(t-t')} \\
+ \quad & f_\alpha(\varepsilon)\langle 0,n|\rho(t)|0,m\rangle\langle 0,m|1,m'\rangle\langle 1,m'|0,n'\rangle e^{-i(\varepsilon-\varepsilon_{1m'}+\varepsilon_{0m})(t-t')} \\
- \quad & \bar{f}_\alpha(\varepsilon)\langle 1,m|\rho(t)|1,m'\rangle\langle 0,n|1,m\rangle\langle 1,m'|0,n'\rangle e^{-i(\varepsilon-\varepsilon_{1m}+\varepsilon_{0n})(t-t')} \\
- \quad & \bar{f}_\alpha(\varepsilon)\langle 1,m|\rho(t)|1,m'\rangle\langle 0,n|1,m\rangle\langle 1,m'|0,n'\rangle e^{i(\varepsilon-\varepsilon_{1m'}+\varepsilon_{0n'})(t-t')}\end{aligned} \tag{1.6.6}$$

and a corresponding equation for the $\langle 1, n|\rho(t)|1, n'\rangle$. Again, the Franck-Condon Factors

$$\langle 0, n|1, m\rangle \tag{1.6.7}$$

are determined by the overlap of the vibrational wave functions before and after tunneling of one electron, but they now have to be calculated numerically. Some Franck-Condon factors are shown in Fig. 1.5(b). As a function of Ω, there are two different regimes where either τ_{11} or τ_{21} is dominating. The sudden rise of τ_{11} is due to the level anti-crossing after which the shape of the first eigenstate resembles the harmonic oscillator ground state and vice versa for τ_{21} and the second eigenstate. Also the sign of the τ_{ij} has to be taken into account contrary to the usual rate equation approach where the Franck-Condon factors occur as squared values only.

1.6.4 Vibrational Coherences and Electronic Noise

The vibrational coherence (due to the level splitting) can be extracted from the electronic noise spectrum $S(\omega)$. This quantity can also be calculated from the Master equation. We calculate the frequency dependent noise from the expression (which we do not derived in these Lectures)

$$S_{RR}(\omega) = \langle \mathcal{I}_R\rangle - 2\mathrm{Re}\langle \mathcal{I}_\mathrm{R}\mathcal{R}(\omega)\mathcal{I}_\mathrm{R}\rangle, \tag{1.6.8}$$

where $\mathcal{I}_R$ is the part of the Liouvillian that generates a quantum jump (an electron tunneling to the, e.g., right reservoir), $\mathcal{R}(\omega)$ is the pseudo-inverse of the Liouvillian $\mathcal{L}$ and $\langle \bullet\rangle = Tr[\bullet\rho_{stat}]$. For simplicity, we only calculate the noise contribution in the right reservoir which (together with the contribution from the left reservoir) is sufficient to obtain the noise for strongly asymmetric capacitance coefficients.

Figs. 1.6(b)&(c) demonstrate that the noise is indeed extremely sensitive to changes in the energy level spectrum of the resonator. The level splitting close to the avoided level crossing becomes visible as the appearance of a feature in $S(\omega)$ at frequencies ω close to the corresponding Bohr frequencies (level splitting in the vibrational spectrum, Fig. 1.6(b) inset). The electronic noise thus acts as a direct probe of vibrational coherence. We point out that the appearance of non-trivial spectral information in $S(\omega)$ is due to retaining the non-diagonal elements in the Master equation. In order to emphasize this point, we have compared our results with a corresponding calculation where these elements were set to zero (Fig. 1.6(b)).(not discussed here).

1.7 Electronic Damping of an Oscillator

We now change our point of view and direct our attention on the oscillator. In our model with a single molecular level and a single phonon mode, we split the

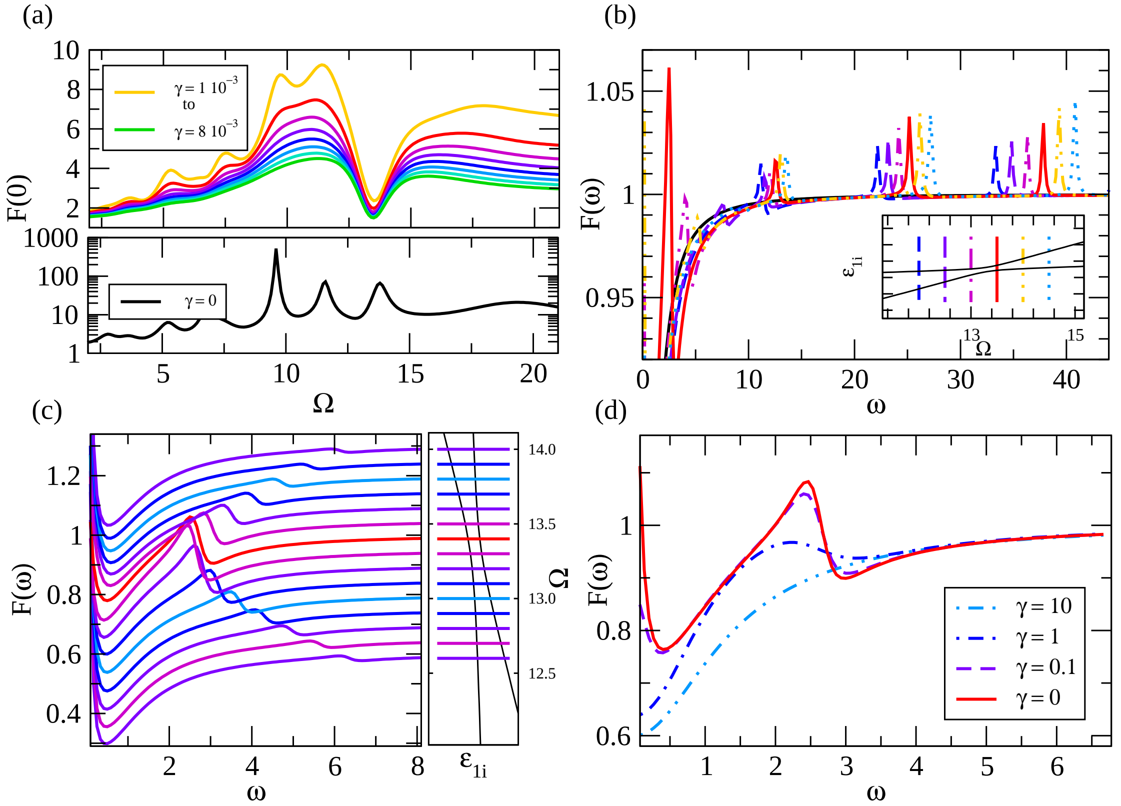

Figure 1.6: (color online). **(a)** Zero Frequency Fano factor for zero damping (lower frame) and several damping strength $\gamma \in [10^{-3}, 810^{-3}]$ (upper frame). **(b)** Frequency dependent Fano factor $F(\omega) = S(\omega)/\langle\mathcal{I}\rangle$ for systems with eigenfrequencies Ω as indicated in the inset, $V_{Bias} = V_{Gate} = 30$. Coupling parameters are $\Gamma_L = 1/2\pi$ and $\Gamma_R = 1/4\pi$. For comparison the case where only diagonal elements of the Liovillian are considered (black line). **(c)** As (b). The sensitivity of the noise to the level anti-crossing is seen as a growing and flattening peak at the frequency corresponding to the level spacing for eigenfrequencies scanning through the anti-crossing point. The oscillator eigenfrequency of each line is indicated by the right frame as well as its position with respect to the avoided-crossing. The scale of the axis refers to the oscillator frequency at the level anti-crossing point $\Omega = 13.4$ (red line) the other lines have an offset of $\pm n0.05$. **(d)** $F(\omega)$ for $\Omega = 13.4$ and several damping strength γ. For high damping the peak at the level spacing disappears and the noise spectrum resembles the single resonant level result.

Hamiltonian into 'system' (oscillator) and 'bath' (electrons) according to

$$\mathcal{H} = \mathcal{H}_S + \mathcal{H}_{SB} + \mathcal{H}_B \tag{1.7.1}$$

$$\mathcal{H}_S \equiv \omega_0 a^\dagger a = \frac{p^2}{2M} + \frac{1}{2} M \omega_0^2 q^2 \tag{1.7.2}$$

$$\mathcal{H}_B \equiv \mathcal{H}_{FA} \equiv \sum_{k,\alpha=L/R} \varepsilon_{k,\alpha} c^\dagger_{k\alpha} c_{k\alpha} + \sum_{k\alpha} (V_{k\alpha} c^\dagger_{k\alpha} d + H.c.) + \varepsilon d^\dagger d \tag{1.7.3}$$

$$\mathcal{H}_{SB} \equiv \lambda' \omega_0 (a + a^\dagger) d^\dagger d = \lambda q d^\dagger d. \tag{1.7.4}$$

Here, we neglect the electron spin in order to simplify things. We also renamed the coupling constant in '$a + a^\dagger$ notation' in $\mathcal{H}_{SB}$ into λ' so that we can use λ as the coupling constant in q (oscillator position) notation. The 'bath' Hamiltonian $\mathcal{H}_B$ is the Hamiltonian $\mathcal{H}_{FA}$ of the *Fano-Anderson* model, which is an exactly solvable model for electrons tunneling between two reservoirs $\alpha = L/R$ through a single level ε.

Rather than being interested in electronic transport in the presence of a phonon mode, we now focus on the oscillations of the phonon mode in presence of electron tunneling on and off the molecular level ε. The idea is to 'integrate out' the electrons altogether and thus arrive at an effective theory for the oscillator. This programme can be carried out within the framework of *Feynman-Vernon influence functional theory* [3]

1.7.1 Influence-functional Theory

Let us consider the time-evolution of a density operator $\chi(t)$ for a generic system-bath Hamiltonian,

$$H \equiv H_S + H_B + H_{SB}, \chi(t) = e^{-iHt}\chi(t=0)e^{iHt}. \tag{1.7.5}$$

For the moment, let us assume that the system has one degree of freedom q and the bath the degree of freedom x (the generalisation to many bath degrees of freedom x_i is straightforward). We then use a representation of $\chi(t)$ in spatial coordinates,

$$\begin{aligned} \langle x, q|\chi(t)|q', x'\rangle &= \int dq_0 dq_0' dx_0 dx_0' \langle x, q|e^{-iHt}|q_0, x_0\rangle\langle x_0 q_0|\chi(t=0)|q_0', x_0'\rangle \\ &\times \langle x_0' q_0'|e^{iHt}|q', x'\rangle. \end{aligned} \tag{1.7.6}$$

We trace out the bath degree of freedoms to obtain an effective density matrix

$$\rho(t) \equiv \mathrm{Tr}_{\mathrm{B}}\chi(t) \tag{1.7.7}$$

of the system,

$$\begin{aligned} \langle q|\rho(t)|q'\rangle &= \int dq_0 dq_0' dx_0 dx_0' dx \langle x, q|e^{-iHt}|q_0, x_0\rangle\langle x_0 q_0|\chi(t=0)|q_0', x_0'\rangle \\ &\times \langle x_0' q_0'|e^{iHt}|q', x\rangle. \end{aligned} \tag{1.7.8}$$

Now we realise that the Hamiltonian $H \equiv H_S + H_B + H_{SB}$ induces a classical action $S_{\text{total}} \equiv S_S[q] + S_B[x] + S_{SB}[xq]$, where in the following for notational simplicity we omit indices at the three S. We use the path integral representation for the propagator matrix elements,

$$\begin{aligned}
\langle q|\rho(t)|q'\rangle &= \int dq_0 dq_0' \langle q_0|\rho(0)|q_0'\rangle \int_{q_0}^{q} \mathcal{D}q \int_{q_0'}^{q'} \mathcal{D}^* q' \exp\left[i\left(S[q]-S[q']\right)\right] \underline{\mathcal{F}[q(t'),q'(t')]} \\
\mathcal{F}[q(t'),q'(t')] &\equiv \int dx_0 dx_0' dx \langle x_0|\rho_B|x_0'\rangle \\
&\times \int_{x_0}^{x} \mathcal{D}x \int_{x_0'}^{x} \mathcal{D}^* x' \exp\left[i\left(S[x]+S[xq]\right) - i\left(S[x']+S[x'q']\right)\right]
\end{aligned}$$

- In the original Feynman-Vernon method, one assumes *a factorising initial condition* $\chi(t=0)=\rho(0)\otimes\rho_B$, although that can be generalised to non-factorising initial density matrices $\chi(t=0)$, cf. for example H. Grabert, P. Schramm, G. L. Ingold, Phys. Rep. **168**, 115 (1988), or the book by Weiss.
- The functional $\mathcal{F}[q(t'),q'(t')]$ is called **influence functional** . It describes the effect of the bath on the time-evolution of the system density matrix.
- For zero system-bath coupling $H_{SB}=0$, $\mathcal{F}[q(t'),q'(t')]=1$

Let us assume that we can write

$$H_{SB} = H_{SB}[q] = f(\hat{q})\hat{X} \tag{1.7.9}$$

with some given bath operator $\hat{X}$ and some given function $f(\hat{q})$ of the system coordinate $\hat{q}$. The influence functional can then be written as

$$\begin{aligned}
\mathcal{F}[q(t'),q'(t')] &\equiv \int dx_0 dx_0' dx \langle x_0|\rho_B|x_0'\rangle \\
&\times \int_{x_0}^{x} \mathcal{D}x \exp\left[i\left(S[x]+S[xq]\right)\right] \int_{x_0'}^{x} \mathcal{D}^* x' \exp\left[-i\left(S[x']+S[x'q']\right)\right] \\
&= \int dx_0 dx_0' dx \langle x_0|\rho_B|x_0'\rangle \langle x|U_B[q]x_0\rangle \left[\langle x|U_B[q']x_0'\rangle\right]^* \\
&= \mathrm{Tr_B}\left(\rho_B U_B^\dagger[q'] U_B[q]\right),
\end{aligned} \tag{1.7.10}$$

where $U_B[q]$ is the unitary time-evolution operator for the time-dependent Hamiltonian $H_B+H_{SB}[q]$ with a given $q(t'), 0\le t'\le t$. Note that $q(t')$ and $q'(t')$ are independent paths, they enter as 'external' parameters into the influence functional which then in the final expression for $\langle q|\rho(t)|q'\rangle$ is integrated over all paths $q(t')$ and $q'(t')$. This form is useful to recognise general properties of $\mathcal{F}[q(t'),q'(t')]$,

- $q(t')=q'(t') \rightsquigarrow \mathcal{F}[q(t'),q'(t')]=1$.
- $|\mathcal{F}[q(t'),q'(t')]|\le 1$.

The

$$\boxed{\begin{array}{c}\text{Operator Form of Influence Functional}\\ \mathcal{F}[q(t'),q'(t')]\equiv \mathrm{Tr_B}\left(\rho_B U_B^\dagger[q']U_B[q]\right),\end{array}} \qquad (1.7.11)$$

is particularly useful for discussing the coupling to other baths (spin-baths, Fermi baths etc.)

1.7.2 Non-equilibrium Damping: Quasi-Classical Approximation

In the quasi-classical approximation, one expands around deviations from the 'diagonal' in the double path integrals, i.e. paths $q(t')=q'(t')$. This is achieved by introducing center-of-mass and relative coordinates,

$$x_t=\frac{1}{2}\left(q_t+q_t'\right),\quad y_t=q_t-q_t', \qquad (1.7.12)$$

where we introduce a shorthand notation $x_t=x(t)$ etc.

The system-bath coupling in our model then becomes

$$\mathcal{H}_{SB}[q_{t'}] \;=\; \mathcal{H}_{SB}\left[x_{t'}+\frac{y_{t'}}{2}\right]=\lambda x_{t'}+\frac{y_{t'}}{2}d^\dagger d. \qquad (1.7.13)$$

However, if the bath is the Fano-Anderson model, $\mathcal{H}_B\equiv\mathcal{H}_{FA}$, something important is missing: the effect of the bath (i.e. the electrons) on the oscillator will depend on the oscillator coordinate q, because the electronic energy depends on q as $(\varepsilon+\lambda q)d^\dagger d$. This would mean that we actually have to regard the coupling term $\mathcal{H}_{SB}[q_{t'}]$ as part of the bath. The 'bath'

$$\mathcal{H}_{FA}+\lambda q d^\dagger d, \qquad (1.7.14)$$

however, is a very difficult bath as the effective level energy wildy fluctuates, and there is no hope to integrate out the electrons with Eq. (1.7.14) exactly.

Mozyrsky, Hastings and Martin [4] therefore came up with the idea to use an adiabatic approximation (Born-Oppenheimer approximation) for the case where the oscillator moves much slower than the electrons tunnel on and off the level,

$$\omega_0\ll\Gamma_R,\Gamma_L,V, \qquad (1.7.15)$$

where V is the bias voltage.

Let us follow the time-evolution of the oscillator over a short time interval, starting at its density matrix center-of-mass coordinate x_0 at time $t=0$. Let us assume we just want a very short time interval $[0,t]$ in which the oscillator barely moves, in which however many electronic tunnel events happen. The electrons will permanently try to shift the oscillator equilibrium position via the polaronic shift, in particular if the coupling λ is strong. We then write

$$\mathcal{H}_B + \mathcal{H}_{SB}[q_{t'}] \equiv \mathcal{H}_{FA} + \lambda q_{t'} d^\dagger d = \underbrace{\mathcal{H}_{FA} + \lambda x_0 d^\dagger d}_{\bar{\mathcal{H}}_B} + \underbrace{\lambda \left[(t'\dot{x}_0 + ...) + \frac{y_{t'}}{2} \right] d^\dagger d}_{\bar{\mathcal{H}}_{SB}} \qquad (1.7.16)$$

which means that we shift the 'main part' x_0 of the oscillator coordinate into the bath Hamiltonian $\bar{\mathcal{H}}_B$ which thus acquires the desired dependence on the oscillator coordinate, and we shift the 'fluctuating' part (deviations from x_0 and the whole quantum off-diagonal coordinate $y_{t'}$ into the system-bath coupling $\bar{\mathcal{H}}_{SB}$.

We will now do a 'self-consistent' calculation: first, calculate the double path integral and the influence functional with fixed x_0 in $\bar{\mathcal{H}}_B$; then in the resulting expressions replace the fixed x_0 again by the full c.o.m. coordinate x_t. This is a form of Born-Oppenheimer approximation: we first keep the 'nuclei' (the oscillator) fixed ('clamped nuclei approximation') and are thus able to calculate the nuclear potential generated by the electrons, and then use the parametric nuclear coordinates as full nuclear coordinates in the so generated potential.

The propagator J for the density matrix ρ of the oscillator defines the time-evolution,

$$\begin{aligned} \left\langle x + \frac{y}{2} | \rho(t) | x - \frac{y}{2} \right\rangle &= \int dx_0 dy_0 \left\langle x_0 + \frac{y_0}{2} | \rho(0) | x_0 - \frac{y_0}{2} \right\rangle J(x, y, t; x_0, q_0) \\ J(x, y, t; x_0, y_0) &= \int_{x_0}^{x} \mathcal{D}x \int_{y_0}^{y} \mathcal{D}y \exp\left[i \int_0^t dt' \left(M\dot{x}_{t'}\dot{y}_{t'} - M\omega_0^2 x_{t'} y_{t'} \right) \right] \\ &\times \mathcal{F}[x_{t'}, y_{t'}] \end{aligned} \qquad (1.7.17)$$

The influence functional in a second order cluster expansion in λ is

$$\begin{aligned} \ln \mathcal{F}[x_{t'}, y_{t'}] &= -i\lambda \int_0^t dt' y_{t'} \langle \hat{n}(t') \rangle_{\bar{B}} \\ &- \int_0^t dt' \int_0^{t'} ds \left\{ f_{t'}^+ - f_{t'}^- \right\} \left\{ S(t'-s) f_s^+ - S^*(t'-s) f_s^- \right\} \\ f_{t'}^{\pm} &\equiv \lambda \left[t'\dot{x}_0 + ... \pm \frac{y_{t'}}{2} \right], \quad S(\tau) \equiv \langle \hat{n}_d(\tau) \hat{n}_d(0) \rangle_{\bar{B}}. \end{aligned} \qquad (1.7.18)$$

The only additional approximation now is the Born-Oppenheimer approximation, i.e. we neglect the terms .... in $f_{t'}^{\pm} \equiv \lambda \left[t'\dot{x}_0 + ... \pm \frac{y_{t'}}{2} \right]$. Then the influence functional becomes

$$\begin{aligned} \ln \mathcal{F}[x_{t'}, y_{t'}] &= -i\lambda \int_0^t dt' y_{t'} \langle \hat{n}_d \rangle_{\bar{B}} - \lambda^2 \int_0^t dt' \int_0^{t'} ds y_{t'} y_s \mathrm{Re} S(t'-s) \\ &- 2i\lambda^2 \dot{x}_0 \int_0^t dt' \int_0^{t'} ds y_{t'} s \mathrm{Im} S(t'-s). \end{aligned} \qquad (1.7.19)$$

We will now reckognize the physical meaning of these expressions: we can rearrange the whole propagator into

$$
\begin{aligned}
J_{\mathrm{sc}}(x,y,t;x_0,y_0) &= \int_{x_0}^{x}\mathcal{D}x\int_{y_0}^{y}\mathcal{D}y\exp\left[iM(\dot{x}_t y-\dot{x}_0 y_0)\right]\times\\
\times\quad \exp&\left[-i\int_0^t dt' y_{t'}K(t')-\lambda^2\int_0^t dt'\int_0^{t'} ds y_{t'}y_s\mathrm{Re}\langle\hat{n}_d(t'-s)\hat{n}_d(0)\rangle_{\bar{B}}\right]\\
K(t') &\equiv M\ddot{x}_{t'}+M\omega_0^2x_{t'}+\lambda\langle\hat{n}_d\rangle_{\bar{B}}+2\int_0^{t'} ds\lambda^2 s\mathrm{Im}\langle\hat{n}_d(t'-s)\hat{n}_d(0)\rangle_{\bar{B}}\dot{x}_0
\end{aligned}
\tag{1.7.20}
$$

This is an interesting expression: it is essentially a 'huge' Gaussian integral centered around $K=0$ with a width described by quadratic, i.e. Gaussian fluctuations, the strength of which is determined by the real part of the correlation function $\langle\hat{n}(t'-s)\hat{n}(0)\rangle_{\bar{B}}$. The condition $K=0$ now is the desired differential equation of our oscillator,

$$
M\ddot{x}_{t'}+M\omega_0^2x_{t'}+\lambda\langle\hat{n}_d\rangle_{\bar{B}}+2\int_0^{t'} ds\lambda^2 s\mathrm{Im}\langle\hat{n}_d(t'-s)\hat{n}_d(0)\rangle_{\bar{B}}\dot{x}_0=0, \tag{1.7.21}
$$

where $-\lambda\langle\hat{n}\rangle_{\bar{B}}$ is an extra force on top of $M\omega_0^2x_{t'}$. We can calculate the occupation, e.g. with the help of Green's functions,

$$
\langle n_d\rangle(x) \;=\; -i\int\frac{d\omega}{2\pi}G^{<}_{dd}(\omega)=\int\frac{d\omega}{2\pi}\frac{\Gamma_Lf_L(\omega)+\Gamma_Rf_R(\omega)}{(\omega-\varepsilon-\lambda x)^2+\frac{1}{4}(\Gamma_L+\Gamma_R)^2} \tag{1.7.22}
$$

For $\Gamma_L=\Gamma_R=\Gamma$, zero temperature $T=0$ and $\mu_L=V/2=-\mu_R$, we have

$$
\begin{aligned}
\langle n_d\rangle(x) &= =\Gamma\int\frac{d\omega}{2\pi}\frac{\theta(V/2-\omega)+\theta(-V/2-\omega)}{(\omega-\varepsilon-\lambda x)^2+\Gamma^2} && (1.7.23)\\
&= -\frac{1}{2\pi}\left[\arctan\frac{\varepsilon+\lambda x-V/2}{\Gamma}+\arctan\frac{\varepsilon+\lambda x+V/2}{\Gamma}-\pi\right] && (1.7.24)\\
& && (1.7.25)
\end{aligned}
$$

In the spirit of the Born-Oppenheimer approximation, one would now replace the constant x_0 and $\dot{x}_0$ by time-dependent expressions, thus leading to

$$
M\ddot{x}_{t'}+M\omega_0^2x_{t'}+\lambda\langle\hat{n}_d\rangle(x_{t'})+2\int_0^{t'} ds\lambda^2 s\mathrm{Im}\langle\hat{n}_d(t'-s)\hat{n}_d(0)\rangle_{\bar{B}}\dot{x}_s=0. \tag{1.7.26}
$$

We see that there is then a retarded friction force coupling to the velocity $\dot{x}_s$ of the oscillator. The oscillator furthermore moves in an *effective potential*, $U_{\mathrm{eff}}(x)$

and is subject to an effective force $F_{\rm eff} = -U'_{\rm eff}(x)$

$$U_{\rm eff}(x) = \frac{1}{2}M\omega_0^2 x^2 + \int_0^x dx' \lambda \langle n_d \rangle (x'). \qquad (1.7.27)$$

Depending on the position of the level ε, the bias voltage V, the coupling strength λ, the tunnel rate Γ, and the bare mass and frequency of the oscillator, this potential can give rise to interesting *bistabilities*.

2. MANY PHONON MODES AND DISSIPATION

Bulk phonons are often a source of dissipation when they interact with electrons. In metals, the electron–phonon coupling is usually weak. Electron–phonon scattering rates approach zero when the temperature T goes to zero. This is because at $T = 0$, no occupied electronic states states are available above the Fermi level E_F and all states below E_F are occupied. Electron-phonon scattering would be only possible by absorption of phonons which however is proportional to the Bose distribution $n_B(\omega) = [\exp(\hbar\omega/k_BT) - 1]^{-1}$ which vanishes ($\omega > 0$) at zero temperature.

In electronic few-level systems, electron-phonon scattering is however possible even at zero temperature in the form of *spontaneous emission* of phonons. In electron transport experiments, this has been observed, for example in coupled quantum dots.

2.1 Phonons in Double Quantum Dots

Double quantum dots are simple charge qubits and thus candidates for quantum logic gates. Let us construct a coupled quantum dot model by taking into account: 1. strong interactions 2. coupling between the dots 3. coupling to the external world (leads) 4. coupling to other degrees of freedom such as bosonic excitations, photons, phonons.

No–one has succeeded to reliably calculate transport properties of such a model in the whole parameter space. In the following, we again use our Master equation formalism and treat the coupling to the leads in lowest order perturbation theory ($T \gg T_K$, no Kondo physics). Coulomb effects are also dealt with in an extremely simplified manner: Assume two dots coupled by a tunnel barrier. The Coulomb charging energy U in small dots is typically $U \sim 1$ meV $\gg V_{\text{transport}} = (\mu_L - \mu_R)/e$: assuming there are N electrons in the left and M electrons in the right dot $\rightsquigarrow$ ground state $|0\rangle = |N, M\rangle$. The additional transport electron is either on the left or on the right dot $\rightsquigarrow$ states $|L\rangle = |N + 1, M\rangle$,$|R\rangle = |N, M + 1\rangle$. Therefore, only three states are involved! Nevertheless, including dissipation, microwave radiation etc this still is complicated enough to be an interesting model.

2.1.1 Isolated Double Dot

We describe the space spanned by the two states L and R with the help of (pseudo) spin Pauli matrices: The Hamiltonian for this subspace is

$$H_0 = \frac{\varepsilon}{2}\sigma_z + T_c\sigma_x, \tag{2.1.1}$$

where $\sigma_z = |L\rangle\langle L| - |R\rangle\langle R|$ and $\sigma_x = |L\rangle\langle R| + |R\rangle\langle L|$. Here, $\varepsilon = \varepsilon_L - \varepsilon_R$ is the difference of the ground state energies of $|L\rangle$ and $|R\rangle$, and T_c describes the coupling between the two dots.

The eigenvectors and energy eigenvalues of H_0 are

$$\begin{aligned} |\pm\rangle &= \frac{1}{N_\pm}\left[\pm 2T_c|L\rangle + (\Delta \mp \varepsilon)|R\rangle\right], \quad N_\pm := \sqrt{4|T_c|^2 + (\Delta \mp \varepsilon)^2} \\ \varepsilon_\pm &:= \pm\frac{1}{2}\Delta, \quad \Delta := \sqrt{\varepsilon^2 + 4|T_c|^2}. \end{aligned} \tag{2.1.2}$$

In microwave experiments, the square–root form of Δ was detected in 1998.

2.1.2 Coupling to Phonons

We describe the coupling to phonons by a Hamiltonian

$$H = \frac{\varepsilon}{2}\sigma_z + T_c\sigma_x + \frac{1}{2}\sigma_z A + \sum_{\mathbf{Q}} \omega_Q a^\dagger_{\mathbf{Q}} a_{\mathbf{Q}}, \quad A := \sum_{\mathbf{Q}} g_Q \left(a_{-\mathbf{Q}} + a^\dagger_{\mathbf{Q}}\right) \tag{2.1.3}$$

Here, ω_Q are the frequencies of phonons, and the g_Q denote interaction constants. Although not exactly solvable, the model is quite well understood for closed systems [5] (isolated dots with one additional electron). The coupling to external leads offers the possibility to study its non–equilibrium properties, such as the inelastic stationary current through the dots.

2.1.3 Equations of Motion

We describe the dynamics of the double dot by a reduced (effective) statistical operator $\rho(t)$. The coupling to the reservoirs is described by the additional Hamiltonian

$$H_{\rm res} + H_V, \quad H_{\rm res} = \sum_k \varepsilon^L_k c^\dagger_k c_k + \sum_k \varepsilon^R_k d^\dagger_k d_k \tag{2.1.4}$$

$$H_V = \sum_k \left(V_k c^\dagger_k s_L + W_k d^\dagger_k s_R + c.c.\right), \quad s_L := |0\rangle\langle L|, \quad s_R := |0\rangle\langle R|. \tag{2.1.5}$$

We start from the Liouville–von Neumann equation for the density operator of the total system (DOT + PHONONS + RESERVOIRS),

$$\frac{d}{dt}\chi(t) = -i[H, \chi(t)]. \tag{2.1.6}$$

The first step: transformation into the interaction picture with respect to $H_0 := H_B + H_{\text{res}}$, $\tilde{O}(t) = e^{iH_0t}Oe^{-iH_0t}$ for any operator O. Write the total Hamiltonian $H = H + V$, and Eq. (2.1.6) becomes

$$\frac{d}{dt}\tilde{\chi}(t) = -i[\tilde{V}(t), \tilde{\chi}(t)]. \tag{2.1.7}$$

Iteration of Eq. (2.1.7),

$$\frac{d}{dt}\tilde{\chi}(t) = -i[\tilde{V}(t), \chi(0)] - \int_0^t dt' \left[\tilde{V}(t), [\tilde{V}(t), \tilde{\chi}(t)]\right]. \tag{2.1.8}$$

We define the effective density operator for the double dot,

$$\rho(t) = \text{Tr}_{\text{res,phonon}}\chi(t). \tag{2.1.9}$$

Now, second order Born and Markov approximation in the perturbation V yields [6, 7]

$$\begin{aligned}
\frac{\partial}{\partial t}\rho_{LL}(t) &= -iT_c\left[\rho_{LR}(t) - \rho_{RL}(t)\right] + \Gamma_L\left[1 - \rho_{LL}(t) - \rho_{RR}(t)\right] \\
\frac{\partial}{\partial t}\rho_{RR}(t) &= -iT_c\left[\rho_{RL}(t) - \rho_{LR}(t)\right] - \Gamma_R\rho_{RR}(t),
\end{aligned}$$

where the tunnel rates are

$$\Gamma_L = 2\pi\sum_k |V_k|^2\delta(\varepsilon_k^L - \varepsilon_L) \quad \Gamma_R = 2\pi\sum_k |W_k|^2\delta(\varepsilon_k^L - \varepsilon_R). \tag{2.1.10}$$

and we allow for tunneling from a left reservoir at rate Γ_L into the left dot, and from the right dot to the right reservoir at rate Γ_R.

For the remaining equation for the off–diagonal element $\rho_{LR} = \rho_{RL}^*$, one has to choose between a perturbation theory in g_Q (weak coupling, PER), or a perturbation theory in T_c in a polaron–transformed frame (strong coupling, POL) . In general, no exact solution of the model is available: this is the case even for coupling to one bosonic mode only ($g_Q \propto \delta_{Q,Q_0}$, Rabi Hamiltonian).

For the spin–boson problem with $\Gamma_{R/L} = 0$, it is well–known that POL is equivalent to a double–path integral 'non–interacting blip approximation' (NIBA) that works well for zero bias $\varepsilon = 0$ but for $\varepsilon \neq 0$ does not coincide with PER at small couplings and low temperatures. It turns out that when comparing both approaches for $\Gamma_{R/L} \neq 0$, one finds nearly perfect agreement for very large $\varepsilon \gg T_c$, a regime that has been tested experimentally recently [8].

The standard Born and Markov approximation with respect to A yields

$$\frac{d}{dt}\rho_{LR}^{\mathrm{PER}}(t) = \left[i\varepsilon - \gamma_p - \Gamma_R/2\right]\rho_{LR}(t) + \left[iT_c - \delta_-\right]\rho_{RR}(t) - \left[iT_c - \delta_+\right]\rho_{LL}(t).$$

Here, the rates are

$$\begin{aligned} \gamma_p &:= 2\pi\frac{T_c^2}{\Delta^2}\rho(\Delta)\coth\left(\beta\Delta/2\right), \quad \delta_\pm := -\frac{\varepsilon T_c}{\Delta^2}\frac{\pi}{2}\rho(\Delta)\coth\left(\beta\Delta/2\right) \mp \frac{T_c}{\Delta}\frac{\pi}{2}\rho(\Delta) \\ \rho(\omega) &:= \sum_{\mathbf{Q}} |g_Q|^2\delta(\omega - \omega_Q). \end{aligned} \tag{2.1.11}$$

where $\Delta := \sqrt{\varepsilon^2 + 4T_c^2}$ is the energy difference of the hybridized levels, and $\beta = 1/k_B T$ the inverse phonon equilibrium bath temperature. Note that beside the off–diagonal decoherence rate γ_p, there appear terms $\propto \delta_\pm$ in the diagonals which below turn out to be important for the stationary current.

On the other hand, the polaron transformation [6] leads to an integral equation

$$\begin{aligned} \rho_{LR}^{POL}(t) &= -\int_0^t dt' e^{i\varepsilon(t-t')}\left[\frac{\Gamma_R}{2}C(t-t')\rho_{LR}(t')\right. \\ &+ \left. iT_c(t')\left\{C(t-t')\rho_{LL}(t') - C^*(t-t')\rho_{RR}(t')\right\}\right], \end{aligned}$$

where

$$C(\tau) := \exp\left\{-\int_0^\infty d\omega \frac{\rho(\omega)}{\omega^2}\left[(1-\cos\omega t)\coth(\beta\omega/2) + i\sin\omega t\right]\right\}. \tag{2.1.12}$$

2.1.4 Stationary Current

Calculated as $I_{\mathrm{stat}} = -e2T_c\mathrm{Im}\hat{\rho}_{LR}(z=0)$ from Laplace transforming the equations of motion;

$$I_{\mathrm{stat}} = \frac{-e\Gamma_L\Gamma_R G_+}{\Gamma_L G_- + (\Gamma_L + \Gamma_R)G_+ - \Gamma_L\Gamma_R}. \tag{2.1.13}$$

has to be used with either the perturbative result (small e–p coupling) or the polaron transformation (small inter–dot coupling),

$$G_\pm^{(\mathrm{PER})} := 2T_c\mathrm{Im}\frac{iT_c - \delta_\pm}{i\varepsilon - \gamma_p - \Gamma_R/2} \tag{2.1.14}$$

or

$$G_{+}^{(\mathrm{POL})} := 2T_c \mathrm{Im}\frac{-iT_cC_\varepsilon}{1+(1/2)\Gamma_R C_\varepsilon}, \quad G_{-}^{(\mathrm{POL})} := 2T_c \mathrm{Im}\frac{-iT_cC^*_{-\varepsilon}}{1+(1/2)\Gamma_R C_\varepsilon}, \tag{2.1.15}$$

where $C_\varepsilon := \int_0^\infty dt e^{i\varepsilon t}C(t)$.

2.1.5 Noise

The Master equation formalism has also been used to calculate the current **noise spectrum** $S(\omega)$ and the Fano Factor $F = S(0)/2eI$. Recent experiments on transport through layers of double quantum dots seem to be in good agreement with these calculations (preprint G. Kießlich et al.).

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